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**"PYRYLIUM AND PYRIDINIUM COMPOUNDS AND  
PORPHYRIN COMPLEXES FOR 2-D MOLECULAR GRIDS"**

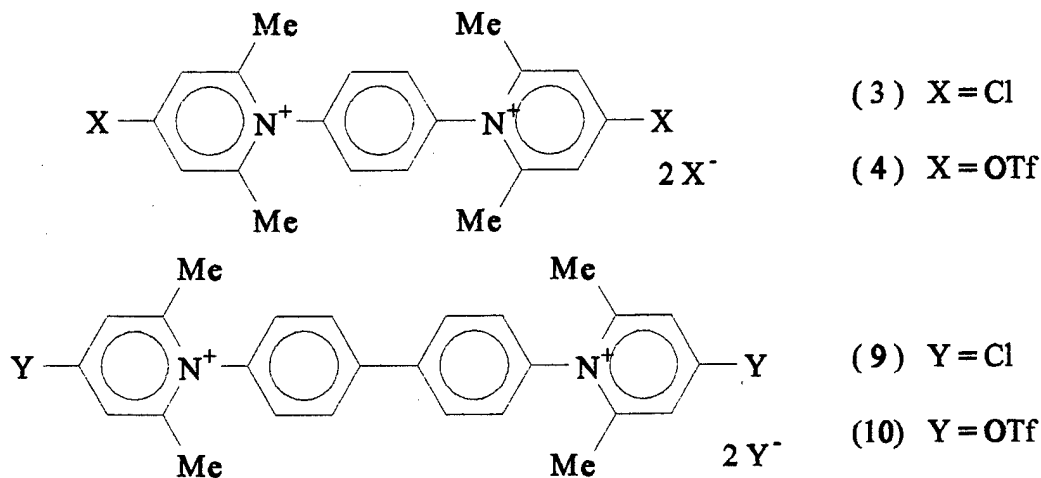
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Albertov 2030, 12840 Prague 2, Czech Republic  
May, 1999

This report contains all information about the project, including the data described in the interim report. In some places these were extended, modified or corrected.

**RESULTS AND DISCUSSION:**

The subject of the reported project was the preparation of some compounds, so called "rods" and "connectors", for the synthesis of molecular grids. These were . It appears that some compounds planned as rods and the methods of their preparation could be used for another purpose as well. We are going to use them in the course of the planned preparation of the molecular electronic elements.

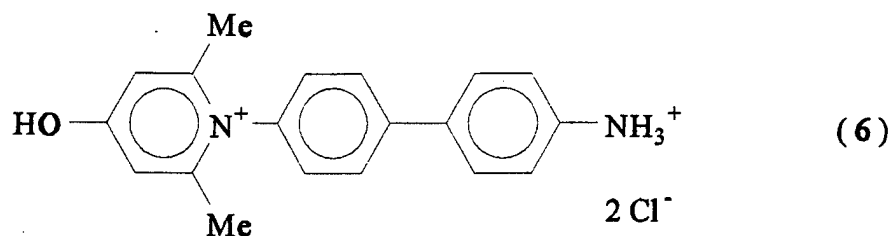
The prepared rods can be divided into two groups. The first of them contains compounds with the following structures.



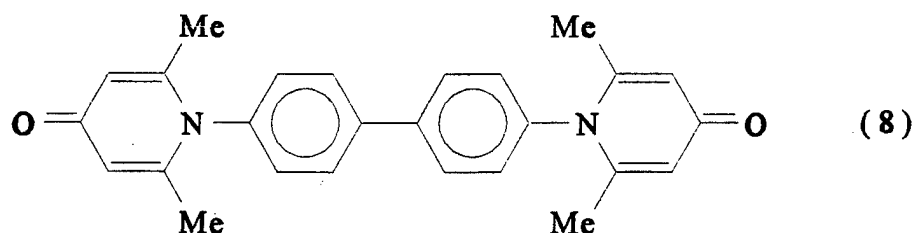
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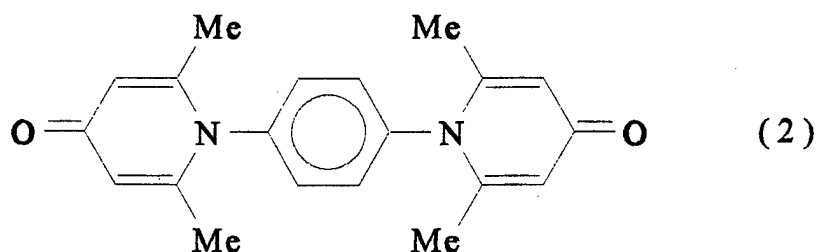
It turned out that the more convenient method of the preparation of these compounds is the reaction of dehydroacetic acid with corresponding amines (*p*-phenylenediamine and benzidine) and subsequent transformation of the created pyridons to pyridinium derivatives. In the benzidine case, only one aminogroup reacted and the precursor (6) of the semirod was obtained.



This compound was reacted with the excess of dehydroacetic acid to give dihydrochloride of the desired 4,4'-bis[2'',6''-dimethylpyridon-(4'')]biphenyl (8).



The direct method, without the isolation of the intermediate (6), was developed as well. In the case of *p*-phenylenediamine, the intermediate was not detected and we got immediately dihydrochloride of 1,4-bis[2',6'-dimethylpyridon-(4')] benzene (2).



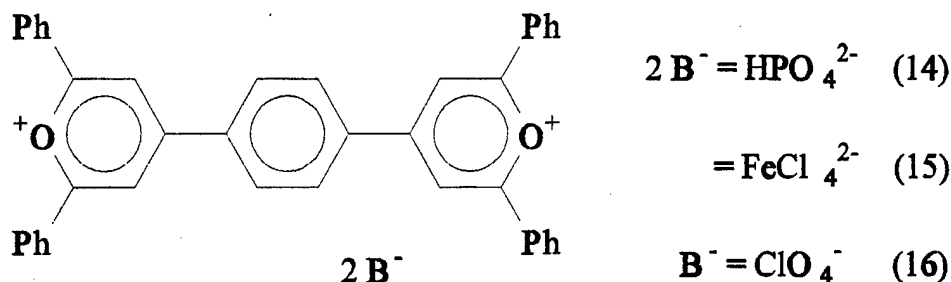
Both pyridon compounds (2 and 8) can be converted to the corresponding chloroderivatives (3 and 9) only under considerably hard conditions and with very reactive chloride. Using halogenides such as thionylchloride or phosphorus trichloride was not successful. However, the reaction was realized by heating with phosphorus pentachloride in tetrachloroethane (reflux). The prepared chlorides 3 and 9 were soluble in water and their water solutions were not liable to hydrolysis.

We also carried out the reaction of the compound 6 with phosphorus pentachloride to get the corresponding semirod. However, these attempts were not successful, as the aminogroup of the compound 6 reacted with  $\text{PCl}_5$  (only insoluble polymer products were

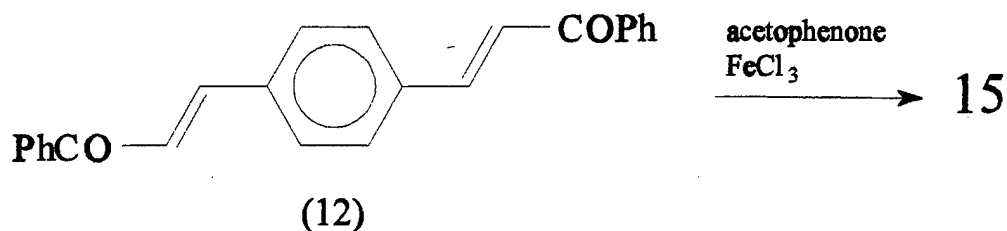
obtained). The reaction could be done only after protecting  $-\text{NH}_2$  group.

Triflates (4 and 10) were prepared from free bases of bis-pyridons (2 and 8) by triflic anhydride. These products are only slightly soluble in water but they can be dissolved in dimethyl sulfoxide.

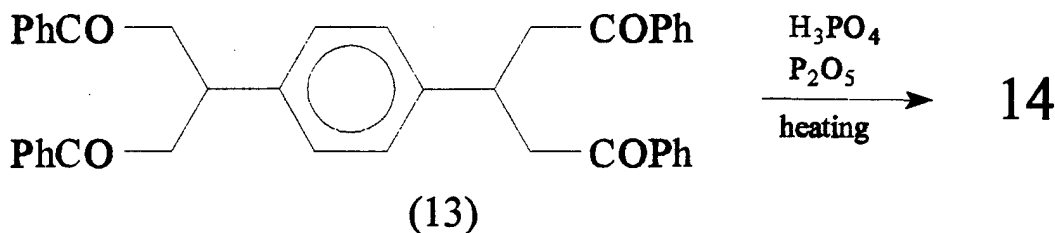
The second group of the rods were the compounds containing pyrylium rings. Pyrylium could react with amines to create pyridinium salts. These compounds had the following structures.



Several methods starting from terephthalaldehyde and acetophenone exist for the preparation of these compounds<sup>1</sup>. We tested them and decided to use a little modified process. The desired compounds were prepared by two different ways. The first was the reaction of 1,4-bis(2-benzoyl-vinyl)benzene<sup>2</sup> (12) with acetophenone and anhydrous ferric chloride. The tetrachloroferrate salt 15 was converted to perchlorate 16 with perchloric acid.



The second way started from *p*-phenylene-bis-3,3'-(1,5-diphenylpentane-1,5-dione)<sup>3</sup> (13), that was heated with the solution of phosphorus pentoxide in phosphoric acid. Hydrogen phosphate 14 was obtained.



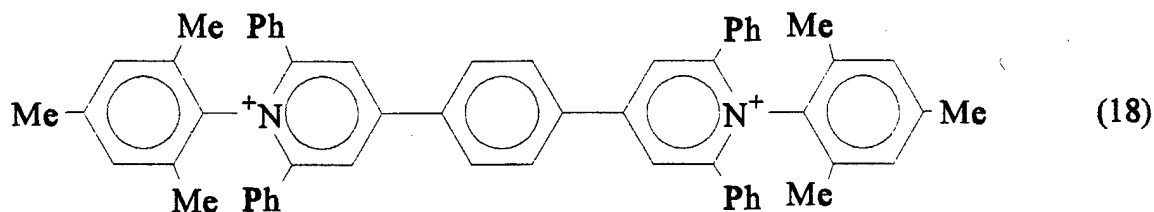
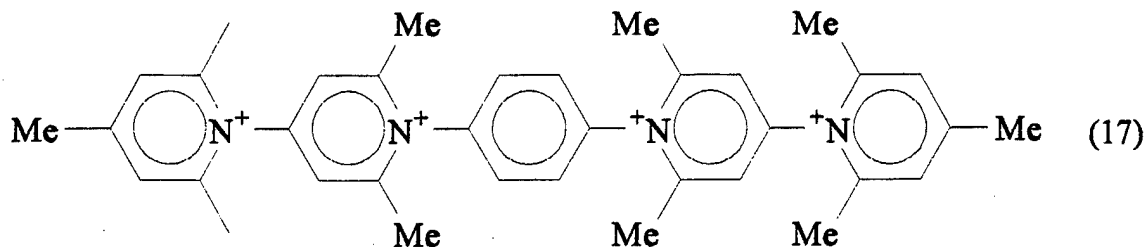
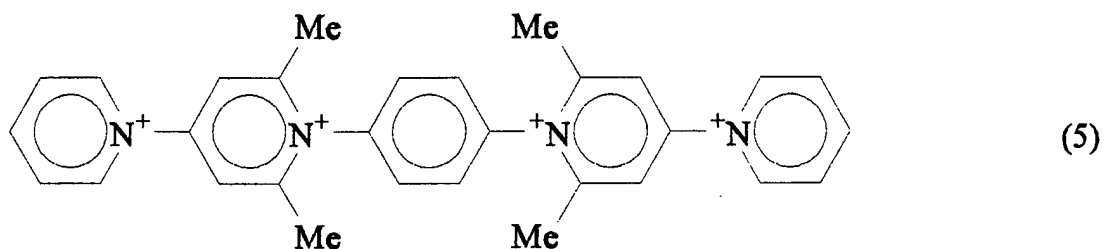
<sup>1</sup> K. Dimroth, Ch. Reichardt *Liebigs Ann. Chem.* **727**, 39 (1969)

<sup>2</sup> H. von Lendenfeld, *Mh. Chem.* **27**, 969 (1906)

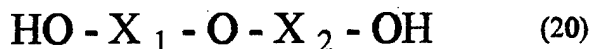
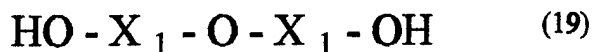
<sup>3</sup> Z. S. Ariyan, B. Mooney, *J. Chem. Soc.* **1962**, 1519

We were also interested in the properties of the reaction product between dichloride **3** and pyridine. Therefore 1,4-bis[2',6'-dimethyl-4'-(pyridinium)-pyridinium] benzene tetrachloride(**5**) was prepared. This reaction ran in water or ethanol. It was slow at room temperature but it took only tens of minutes at 50°C. Analogous reaction between chloride **3** and 2,4,6-collidine was dramatically slower. This reaction gave only an insignificant quantity of the expected product **17** after about 10 hours heating (both components in substance) at 100°C.

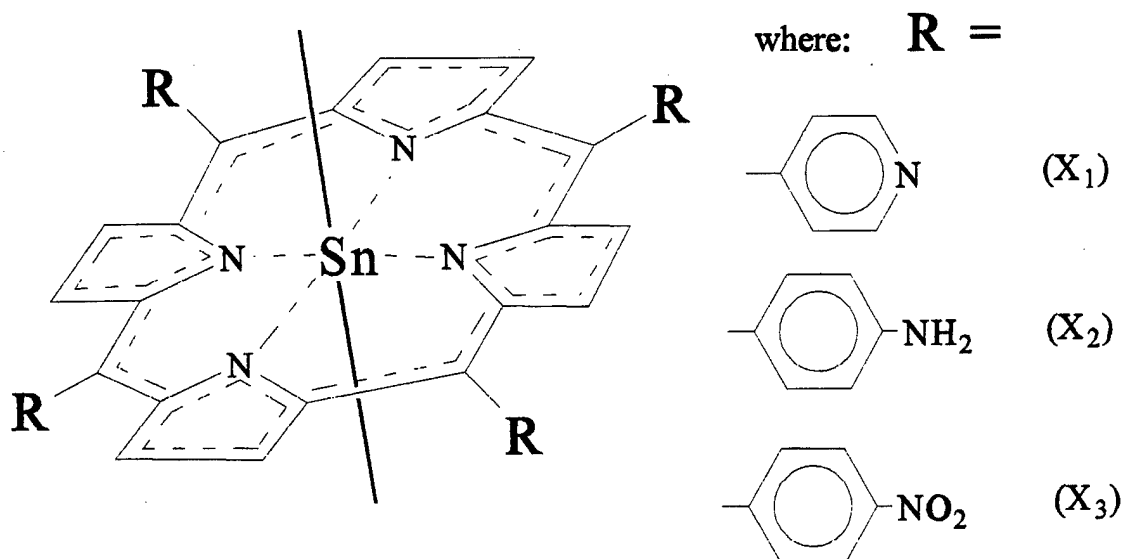
The other compound that we were interested in was the product of the reaction of the pyrylium salt **16** with 2,4,6-trimethylaniline. This procedure was done by heating components in ethanol, or in substance. The compound **18** arose. The products of these reactions had the following structures.



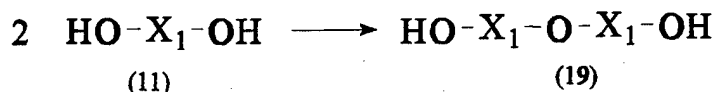
Next part of our research was devoted to the preparation of the "connectors" for the molecular grids construction. These compounds should have the following structures.



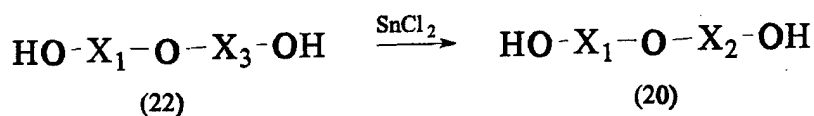
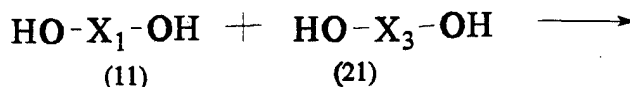
The following figure describes the structures of  $\text{X}_1$  and  $\text{X}_2$  in 19 and 20 and of the group  $\text{X}_3$  which will be used later.



The compound **19** was planned to be prepared from dihydroxo-5,10,15,20-tetra(4'-pyridyl)porphirinatotin(IV) (**11**) by controlled dehydration.



In a similar way, the compound **20** should have been prepared via the mixed dehydration product of **11** and **21** and by the reduction of the nitrogroups to the aminogroups.



Dihydroxo-5,10,15,20-tetra(4'-pyridyl)porphirinatotin(IV) (**11**) was prepared by the reaction between 5,10,15,20-tetra(4'-pyridyl)porphine and tin tetrachloride. The reaction was performed in pyridine to avoid an interaction of unprotected pyridyl groups and  $\text{SnCl}_4$ . Tin tetrachloride created a complex with an excess of pyridine. Only a small part of tin tetrachloride was bonded to tetrapyridylporphine. The reaction was successful, however, the yields were very small (about 10%).

A method for the preparation of porphine complexes of tin(IV) in acetic acid by stannous chloride was proposed earlier<sup>4</sup>. We conjectured, that pyridyl groups could be somewhat protonized in such an environment and their activity for stannous chloride

<sup>4</sup> E. Meinjohans, M. Medal, A. Schleyer, H. Paulsen, K. Bock: *J. Chem. Soc., Perkin Trans. I*, 1996, 985

would be small. This procedure was realized with a yield of approximately 30%.

In both cases the hydroxo derivatives **11** and **21** were obtained. The chloro derivatives were hydrolyzed during isolation and purification (ammonia had to be used to deprotonize the pyridyl groups and to release them from Sn adducts).

Dihydroxo-5,10,15,20-tetra(4'-nitrophenyl)porphirinatin(IV) (**21**) was prepared from 5,10,15,20-tetra(4'-nitrophenyl)porphine and tin tetrachloride in pyridine (stannous chloride is not eligible because of interaction with -NO<sub>2</sub> group). Starting tetranitrophenylporphine was prepared by a known procedure<sup>5</sup> from *p*-nitrobenzaldehyde and pyrrole in the mixture of nitrobenzene and propionic acid.

After dehydration of **11** we got a complex mixture of oligomers and some byproducts. We concentrated our effort mainly on the preparation of compound **19**, where the reaction mixture is simpler than in the case of compound **20**. We tried to separate the reaction mixture products by chromatography on alumina. The mixture of chloroform and methanol was used as the eluent. Different sorts of alumina (neutral and basic with various activities) were tested and the optimal ratio of the solvents was investigated. Attempts were made to add a small quantity of ammonia to the eluent (for neutralization of the acid centres in alumina). However, the reaction products were unstable and they altered in the course of the chromatography separation. In spite of our effort, we have not succeeded in separating the pure components and their determination until the dead-line of this report.

We also tested the reactions of 5,10,15,20-tetra(4'-pyridyl)porphine with chlorides of other metals. For example AlCl<sub>3</sub> in carbon disulfide gave the desired product, but the yield was very small.

## EXPERIMENTAL:

### GENERAL :

Infrared spectra were recorded on a Perkin-Elmer (PE-684) instrument, <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on Varian INOVA 400 instrument. For the <sup>1</sup>H NMR spectra in CDCl<sub>3</sub>, tetramethylsilane was used as internal standard and for the <sup>13</sup>C NMR spectra the signal of CDCl<sub>3</sub> was used { δ(CDCl<sub>3</sub>)=77.0 }. Spectra in D<sub>2</sub>O were referenced to the methyl signal of tert-butylalcohol { δ(t-BuOH, <sup>1</sup>H)=1.25 and δ(t-BuOH, <sup>13</sup>C)=31.6 } and spectra in dimethylsulfoxide-d<sub>6</sub> were referenced to methyl group of solvent { δ(DMSO, <sup>1</sup>H)=2.50 and δ(DMSO, <sup>13</sup>C)=39.50 }. By the measurement in diluted trifluoroacetic acid the signal of CF<sub>3</sub> group was used as standard for the <sup>13</sup>C NMR spectra { δ(CF<sub>3</sub>COOH, <sup>13</sup>C)=164.0 } and <sup>1</sup>H NMR spectra were referenced to signal of small quantity of chloroform, that was added to the solution { δ(CHCl<sub>3</sub>, <sup>1</sup>H)=7.26 }. The rotatory evaporator and the vacuum water pump were used for solvents removing. All substances were of standard commercial quality (Aldrich), solvents were dried and distilled before use. Dehydroacetic acid was prepared from ethyl acetylacetate by the

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<sup>5</sup> A. M. d'A. R. Gonsalves, J. M. T. B. Varejao, M. M. Pereira: *J. Heterocyclic Chem.*, **28**, 635 (1991)

described procedure<sup>6</sup>.

#### SYNTHESIS:

##### 1,4-Bis[2',6'-dimethylpyridon-(4'')]benzene dihydrochloride (1)

A suspension of dehydroacetic acid (5.04 g, 30 mmol) and fresh sublimed *p*-phenylenediamine (1.62 g, 15 mmol) in conc. hydrochloric acid (6 ml) was heated under the reflux for 4 hours. After cooling, the reaction mixture was filtered and the solid material was washed with small portion of ice water (4 ml) and then with acetone (30 ml). The crude product was purified by crystallization from water to yield 1 (4.5 g, 76% th.) as a solid, that does not melt until 300°C.

<sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O) δ ppm 2.33 (12H, s, Me), 7.19 (4H, s, pyridon), 7.83 (4H, s, phenylene)

<sup>13</sup>C NMR (D<sub>2</sub>O) δ ppm 23.37, 115.56, 131.48, 141.81, 158.44, 173.12

##### 1,4-Bis[2',6'-dimethylpyridon-(4'')]benzene (2)

1,4-Bis[2',6'-dimethylpyridon-(4'')]benzene dihydrochloride (1) (3.93 g, 10 mmol) was dissolved in water (40 ml) at 50°C. Water ammonium hydroxide (3 ml, 26% of NH<sub>3</sub>) was slowly added to this solution with stirring and cooling on ice bath. The precipitated solid was filtered off, washed with water and dried in vacuum. Free base 2 was obtained in quantitative yield.

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ ppm 1.88 (12H, s, Me), 6.10 (4H, s, pyridon), 7.64 (4H, s, phenylene)

##### 1,4-Bis[2',6'-dimethyl-4'-chloropyridinium]benzene dichloride (3)

1,4-Bis[2',6'-dimethylpyridon-(4'')]benzene dihydrochloride (1) (1.18 g, 3 mmol), fresh sublimed phosphorus pentachloride (1.56 g, 7.5 mmol) and 1,1,2,2-tetrachloroethane (4 ml) were stirred and heated under the reflux for 4 hours. Then toluene (4 ml) was added and the heating was continued for about 30 min. The temperature of the mixture was left to decrease (to room temp.) and precipitated solid was filtered off. After washing with toluene (5 ml), acetone (10 ml) and diethylether (10 ml), the solid was dried in vacuum.

The crude material was dissolved in 90% ethanol (150 ml), decolorizing carbon was added and the mixture was heated to 50°C. Then it was filtered and poured on column of ionex (15 ml of Amberlyte IRA-410 in chloride cycle) and washed with 90% ethanol (50 ml). The solution was evaporated in vacuum and the rest was recrystallized from ethanol-acetone mixture. Compound 3 was obtained (0.95 g, 74% th.).

<sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O) δ ppm 2.51 (12H, s, Me), 7.95 (4H, s, phenylene), 8.10 (4H, s, pyridinium)

<sup>13</sup>C NMR (D<sub>2</sub>O) δ ppm 23.67, 129.37, 131.03, 141.90, 156.85, 159.30

IR (nujol) ν cm<sup>-1</sup> 1626, 1574, 1508, 1470, 1411, 1287, 1131, 915, 868

##### 1,4-Bis[2',6'-dimethyl-4'-trifluoromethanesulfonylpyridinium]benzene ditriflate (4)

1,4-Bis[2',6'-dimethylpyridon-(4'')]benzene (2) (0.48 g, 1.5 mmol), dry toluene (2 ml) and triflic anhydride (0.68 ml, 4 mmol) were stirred and heated in a sealed tube (2 h, bath temperature 120°C). After cooling, toluene was added (5 ml) and the mixture was filtered. The

<sup>6</sup> Arndt, F.; Hartman, W. W.; Weissberger, A. *Organic Synthesis, Col. Vol. III*, Ed. by Horning, E. C.; N.Y., John Wiley & Sons, Inc., 1967, p. 231.



solid was washed with toluene and dried in vacuum. The compound 4 with small impurities was obtained (0.85 g, 69% th.).

$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  ppm 2.27 (12H, s, Me), 7.28 (4H, s, phenylene), 7.93 (4H, s, pyridinium)

$^{13}\text{C}$  NMR (DMSO- $d_6$ )  $\delta$  ppm 21.32, 113.12, 129.29, 139.40 156.15, 170.84

#### 1,4-Bis[2',6'-dimethyl-4'-(pyridinium)-pyridinium]benzene tetrachloride(5)

1,4-Bis[2',6'-dimethyl-4'-chloropyridinium]benzene dichloride (3) (86 mg, 0.2 mmol) was dissolved in ethanol (10 ml) and pyridine was added (0.2 ml). The solution was heated at 50°C for about 30 min. After cooling, the decolorizing carbon was added and the mixture was filtered and evaporated in vacuum. The rest was recrystallized from ethanol-acetone-diethylether mixture and dried in vacuum. The compound 5 with some impurities was obtained (purity about 80-90% , 40 mg, 34% th.).

$^1\text{H}$  NMR (400 MHz, D $_2$ O)  $\delta$  ppm 2.77 (12H, s, Me), 8.16 (4H, s, phenylene), 8.49 (4H, t, 3-py), 8.65 (4H, s, lutidinium), 9.02 (2H, t, 4-py), 9.45 (4H, d, 2-py)

#### 4-Amino-4'-[2'',6''-dimethylpyridon-(4'')]biphenyl dihydrochloride (6)

The mixture of dehydroacetic acid (3.7 g, 22 mmol), benzidine dihydrochloride (2.7 g, 10.5 mmol) and conc. hydrochloric acid (7 ml) was stirred and heated under the reflux for 4 hours. After cooling to room temperature, the solid was filtered off, washed with water (3 ml) and acetone (10 ml). The crude material (3 g) was recrystallized from ethanol-acetone mixture using decolorizing carbon. 4-Amino-4'-[2'',6''-dimethyl-pyridon-(4'')]biphenyl dihydrochloride (6) was obtained (2.4 g, 67% th.).

$^1\text{H}$  NMR (400 MHz, D $_2$ O)  $\delta$  ppm 2.30 (6H, s, Me), 7.12 (2H, s, pyridon), 7.52 (2H, d, J=8.5 Hz), 7.56 (2H, d, J=8.8 Hz), 7.82 (2H, d, J=8.5Hz), 8.03 (2H, d, J=8.8 Hz)

$^{13}\text{C}$  NMR ( D $_2$ O)  $\delta$  ppm 23.32, 115.56, 125.40, 129.13, 130.65, 131.50, 132.07, 140.08, 141.94, 143.64, 158.59, 173.22

#### 4,4'-Bis[2'',6''-dimethylpyridon-(4'')]biphenyl dihydrochloride (7)

##### Method A

4-Amino-4'-[2'',6''-dimethylpyridon-(4'')]biphenyl dihydrochloride (6) (360 mg, 1 mmol), dehydroacetic acid (250 mg, 1.5 mmol) and conc. hydrochloric acid (1 ml) were heated in a sealed tube at 140°C (bath temp.) for 4 hours. After cooling the tube was opened and the mixture was filtered and washed with ice water (0.5 ml), ethanol (0.5 ml) and acetone (3 ml). By crystallization from ethanol, 4,4'-bis[2'',6''-dimethylpyridon-(4'')]biphenyl dihydrochloride (7) was obtained (260 mg, 55% th.).

##### Method B

Benzidine dihydrochloride (12.9 g, 50 mmol), dehydroacetic acid (16.8 g, 100 mmol) and conc. hydrochloric acid (35 ml) were stirred and heated. The temperature was carefully increased from 80°C to the boiling point of the mixture (carbon dioxide was released) during about 2 hours. Then the mixture was heated under the reflux 2 hours and next portion of dehydroacetic acid (10 g, 60 mmol) with hydrochloric acid (15 ml) was added. After 3 hours boiling and following cooling to room temperature, the solid was filtered off, washed with water (10 ml) and acetone (50 ml), dried and recrystallized from water.

The yield was 16.6 g (71% th.) of the title compound.

$^1\text{H}$  NMR (400 MHz, D $_2$ O)  $\delta$  ppm 2.32 (12H, s, Me), 7.16 (4H, s, pyridon), 7.58 (4H, dt, J=8.5 Hz, J'=2 Hz), 8.05 (4H, dt, J=8.5 Hz, J'=2 Hz)

$^{13}\text{C}$  NMR ( $\text{D}_2\text{O}$ )  $\delta$  ppm 23.34, 115.42, 129.09, 131.50, 140.05, 143.67, 158.79, 172.78

4,4'-Bis[2",6"-dimethylpyridon-(4'')]biphenyl (8)

4,4'-Bis[2",6"-dimethylpyridon-(4'')]biphenyl dihydrochloride (7) (2.35 g, 5 mmol) was dissolved in water (20 ml) at about 50°C and after cooling to room temperature, water ammonium hydroxide (2 ml, 26% of  $\text{NH}_3$ ) was dropped to this solution (with stirring). The precipitated solid was filtered and washed with 1% water ammonia, water and hot ethanol. The material was dried in vacuum. The yield was 1.4 g (71% th.).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 1.97(12H, s, Me), 6.34(4H, s), 7.36(4H, d,  $J=8.3$  Hz), 7.82(4H, d,  $J=8.3$  Hz)

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  ppm 21.54, 117.61, 128.71, 128.86, 139.47, 140.77, 148.59, 179.40

IR (nujol)  $\nu$   $\text{cm}^{-1}$  1639, 1565, 1500, 1421, 1362, 1273, 896, 862, 849

4,4'-bis[2",6"-dimethyl-4"-chloropyridinium]biphenyl dihydrochloride (9)

4,4'-bis[2",6"-dimethylpyridon-(4'')]biphenyl dihydrochloride (7) (141 mg, 0.3 mmol), phosphorus pentachloride (156 mg, 0.75 mmol) and 1,1,2,2-tetrachloroethane (1 ml) were stirred and heated under the reflux for 4 hours. Then toluene was added and the mixture was filtered. The solid was washed with toluene (5 ml), acetone (5 ml) and dried in vacuum.

Ethanol (90%, 10 ml) was added to the material and after stirring and heating to 50°C for 30 min. the insoluble part was filtered off. After decolorizing with active carbon, the ethanolic solution was filtered through ionex column (1 ml, Amberlyte IRA-410 in chloride cycle). The filtrate was evaporated in vacuum and recrystallized from ethanol-acetone mixture. The compound 9 was obtained (100 mg, 66% th.).

$^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$  ppm 2.49 (12H, s, Me), 7.62(4H, dt,  $J=8.8$  Hz,  $J'=2.3$  Hz), 8.05 (4H, s, pyridinium), 8.12 (4H, dt,  $J=8.8$  Hz,  $J'=2.3$  Hz)

$^{13}\text{C}$  NMR ( $\text{D}_2\text{O}$ )  $\delta$  ppm 23.60, 128.00, 129.10, 132.00, 139.80, 144.22, 156.03, 159.70

4,4'-Bis(2',6'-dimethyl-4'-trifluoromethansulfonylpyridinium)biphenyl ditriflate (10)

4,4'-Bis[2",6"-dimethylpyridon-(4'')]biphenyl (9) (0.4 g, 1 mmol) was suspended in dried chloroform (10 ml) and trifluoromethanesulfonic anhydride (0.5 ml, about 3 mmol) was slowly added (with stirring). The mixture was stirred at room temperature for 2 hours and then the temperature was increased to 50°C and the stirring continued next 1 hour. The chloroform was decanted and the insoluble rest was mixed with a small quantity of diethylether. The solid material was filtered off, washed with diethylether and dried.

The yield was 0.5 g (52% th.) of title compound.

$^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  ppm 2.26(12H, s, Me), 7.28(4H, s), 7.73(4H, d,  $J=8.6$  Hz), 8.14(4H, d,  $J=8.6$  Hz)

$^{13}\text{C}$  NMR ( $\text{DMSO}-d_6$ )  $\delta$  ppm 21.45, 113.13, 127.42, 128.92, 138.00, 140.27, 150.37, 170.60

Dihydroxo-5,10,15,20-tetra(4'-pyridyl)porphinatotin(IV) (11)

Method A.

5,10,15,20-tetra(4'-pyridyl)porphine (124 mg, 0.2 mmol) in a tube was dissolved in pyridine (10 ml) and after cooling to -70°C, the anhydrous tin tetrachloride (0.5 g) was added. The tube was sealed and heated to 160°C for 48 hours. The tube was cooled to room temperature and opened. The mixture was filtered and solid was washed with chloroform (20 ml). The filtrate was saturated with  $\text{NH}_3$  and evaporated in vacuum. Chromatography on alumina by chloroform with 2% of methanol and following crystallization from chloroform-hexane mixture afforded the

compound 11 ( 18 mg, 11.7% th.).

#### Method B.

The solution of 5,10,15,20-tetra(4'-pyridyl)porphine (186 mg, 0.3 mmol) in acetic acid (20 ml) was slowly added (during about 6 hours) to the boiling suspension of anhydrous sodium acetate (2 g) and stannous chloride (284 mg, 1.5 mmol) in acetic acid (50 ml). Then the mixture was heated under the reflux for 40 hours. The solvent was evaporated to vacuum and water ammonia was added to the rest and the material was extracted with 50 ml chloroform-methanol mixture (10:1), dried with anhydrous sodium sulfate and concentrated to a small volume. Chromatography on alumina by chloroform-methanol mixture (50:1) gave dihydroxo-5,10,15,20-tetra(4'-pyridyl)porphinatotin(IV) (11), identical with the compound prepared by method A (78 mg, 33.8% th.).  
 $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 8.29 (8H, dd,  $J=4.1$  Hz,  $J'=1.7$  Hz, pyridyl), 9.14 (8H, dd,  $J=4.3$  Hz,  $J'=1.5$  Hz, pyridyl), 9.18 (8H, s, pyrrole)  
 $^{13}\text{C}$  NMR (  $\text{CDCl}_3$ )  $\delta$  ppm 118.87, 129.62, 132.86, 132.97, 146.05, 148.72  
IR (  $\text{CHCl}_3$ ) 3629  $\text{cm}^{-1}$

#### 1,4-bis(2-benzoyl-vinyl)benzene (12)

The solution of sodium hydroxide (1.5 g) in 30% ethanol (20 ml) was slowly dropped with stirring to the solution of terephthalaldehyde (6.7 g, 50 mmol) and acetophenone (12 ml, 103 mmol) in ethanol (120 ml) at about 50°C. The mixture was stirred ten minutes and then it was left to cool to room temperature. The solid material was filtered off, washed with ethanol (about 50 ml) and water (about 100 ml) and dried. Then it was recrystallized from toluene to yield 14.8 g (87.5% th.) of 1,4-bis(2-benzoyl-vinyl)benzene (12) with m.p. 196-9°C [ lit.<sup>2</sup> 201°C ].

#### *p*-Phenylene-bis-3,3'-(1,5-diphenylpentane-1,5-dione) (13)

Sodium hydroxide (2 g) was dissolved in water (20 ml) and to this mixture, the solution of terephthalaldehyde (6.7g, 50 mmol) in ethanol (75 ml) and acetophenone (50 ml, 430 mmol) were added. After 1 hour heating under the reflux the reaction mixture was filtered and precipitated *p*-phenylene-bis-3,3'-(1,5-diphenylpentane-1,5-dione) (13) was washed with ethanol (50 ml), water (200 ml) and dried. The recrystallization from chloroform gave 19.2 g (70% th.) of title compound, melting at 209-10°C [ lit.<sup>3</sup> 187°C ].

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 3.32(4H, dd,  $J_1=6.9$  Hz,  $J_2=16.7$  Hz,  $\text{CH}_2$ ), 3.43(4H, dd,  $J_1=6.9$  Hz,  $J_2=16.7$  Hz,  $\text{CH}_2$ ), 4.02(2H, q,  $J=6.9$  Hz, CH), 7.42(8H, tm,  $J\sim 7.5$  Hz, *m*-Ph), 7.52(4H, tm,  $J\sim 7.5$  Hz, *p*-Ph), 7.91(8H, dm,  $J\sim 7$  Hz, *o*-Ph).

#### *p*-Phenylene-bis-4,4'-(2,6-diphenyl-pyrylium-hydrogenphosphate) (14)

*p*-Phenylene-bis-3,3'-(1,5-diphenylpentane-1,5-dione) (5.5 g, 10 mmol) was added with stirring to the cold solution of phosphorus pentoxide (60 g) in 85% phosphoric acid (40 ml). The mixture was heated to 50°C overnight and then it was poured to water (200 ml). Precipitated phosphate was washed with water (100 ml), ethanol (100 ml) and diethylether (100 ml). It gave 4.4g of *p*-phenylene-bis-4,4'-(2,6-diphenyl-pyrylium-hydrogenphosphate) 14 with a little quantity of impurities, that can be crystallized from dilute trifluoroacetic acid.

$^1\text{H}$  NMR (400 MHz,  $\text{CF}_3\text{COOH} + \text{D}_2\text{O}$ , 2:1)  $\delta$  ppm 7.63(8H, t,  $J=7.3$  Hz, *m*-Ph), 7.74(4H, t,  $J=7.2$  Hz, *p*-Ph), 8.21(8H, d,  $J=7.9$  Hz, *o*-Ph), 8.31(4H, s, Phenylene), 8.51(4H, s, Pyrylium)

#### *p*-Phenylene-bis-4,4'-(2,6-diphenyl-pyrylium-tetrachloroferrate) (15)

1,4-bis(2-benzoyl-vinyl)benzene (6.8 g, 20 mmol) was dissolved in the mixture of acetophenone (7 ml, 60 mmol), acetanhydride (150 ml) and carbon disulfide (100 ml) with stirring and gentle

heating. Anhydrous sublimed ferric chloride (25 g) was slowly added in a few parts with stirring. The reaction mixture was boiled under the reflux 3.5 hours and left to stand two days in the refrigerator. Insoluble part was filtered and washed with diethylether (200 ml) to yield 2.0 g (about 9% th.) of *p*-phenylene-bis-4,4'-(2,6-diphenyl-pyrylium-tetrachloroferrate) (15), which was used for preparation of perchlorate.

*p*-Phenylene-bis-4,4'-(2,6-diphenyl-pyrylium-perchlorate) (16)

was prepared by adding 70% perchloric acid (2 ml) to the solution of *p*-phenylene-bis-4,4'-(2,6-diphenyl-pyrylium-tetrachloroferrate) (1 g) in 30% acetic acid (100 ml). The precipitated material was washed with water (100 ml) and recrystallized from dilute trifluoroacetic acid. The yield was 0.7 g (89% th.).

<sup>1</sup>H NMR (400 MHz, CF<sub>3</sub>COOH + D<sub>2</sub>O, 2:1) δ ppm 7.63 (8H, t, J=7.8 Hz, *m*-Ph), 7.74 (4H, t, J=7.5 Hz, *p*-Ph), 8.22 (8H, d, J=7.8 Hz, *o*-Ph), 8.30 (4H, s, Phenylene), 8.53 (4H, s, Pyrylium)

<sup>13</sup>C NMR (CF<sub>3</sub>COOH + D<sub>2</sub>O, 2:1) δ ppm 131.37, 131.68, 132.46, 133.47, 133.72, 139.94, 141.75, 168.61, 176.11

*p*-Phenylene-bis-[N-(2,4,6-trimethyl-phenyl)-2,6-diphenyl-pyridinium-perchlorate] (18)

Method A

*p*-Phenylene-bis-4,4'-(2,6-diphenyl-pyrylium-perchlorate) (370 mg, 0.5 mmol) and 2,4,6-trimethylaniline (0.14 ml, 1 mmol) was dissolved in ethanol (20 ml). Sodium acetate (0.1 g) was added to the solution and the mixture was boiled under the reflux for 2 hours and left to stand overnight. The solid material was filtered off, washed with water, ethanol and hot acetic acid and dried. It was obtained 140 mg (29% th.) of title compound.

Method B

*p*-Phenylene-bis-4,4'-(2,6-diphenyl-pyrylium-perchlorate) (185 mg, 0.25 mmol) was heated in substance with 2,4,6-trimethylaniline (0.1 ml, about 0.7 mmol) to 100-110°C for 2 hours. After cooling to room temperature diethylether (5 ml) was added to the mixture and solid material was filtered off. Then it was washed with 1% acetic acid, the small portion of ethanol and finally with diethylether. After drying, 130 mg (71% th.) of title compound was obtained.

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ ppm 1.98(12H, s, Me), 2.13(6H, s, Me), 6.83 (4H, s), 7.44(20H, m, Ph), 8.67(4H,s), 8.91(4H,s)

<sup>13</sup>C NMR (DMSO-d<sub>6</sub>) δ ppm 17.84, 20.54, 127.23, 128.19, 129.10, 129.16, 129.93, 130.70, 131.81, 133.50, 134.57, 136.62, 140.23, 154.79, 155.78